



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Isentropic Compression Loading of HMX and the Pressure-induced Phase Transition at 27 GPa

D. E. Hare, D. B. Reisman, J. J. Dick, J. W.
Forbes

February 27, 2004

Applied Physics Letters

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Isentropic Compression loading of HMX and the pressure-induced phase transition at 27

GPa

D.E. Hare and D.B. Reisman

Lawrence Livermore National Laboratory

Livermore, CA 94551

J.J. Dick

Los Alamos National Laboratory

Los Alamos, NM 87545

J.W. Forbes

University of Maryland, Dept. of Mechanical Engineering

College Park, MD 20742

Abstract

The 27 GPa pressure-induced epsilon–phi phase transition in HMX is explored using the Isentropic Compression Experiment (ICE) technique at the Sandia National Laboratories Z-machine facility. Our data indicate that this phase transition is sluggish and if it does occur to any extent under the time scales (200 – 500 ns) and strain rates (5×10^5) typical of ICE loading conditions, the amount of conversion is small.

Introduction

HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) is the main reactive ingredient of many high performance high explosive formulations. There are two phase transitions that have been found along the room temperature isotherm [1]. The one at 12 GPa is from β to ϵ phase and is described as being conformational and martensitic. It apparently occurs without an abrupt volume change. The other one (ϵ to ϕ) is discontinuous, occurs at 27 GPa and is accompanied by a 4 % volume decrease.

The presence of phase transitions may have important consequences for the detailed understanding of detonation in HMX and its formulations. For example the peak pressure of the detonation wave will depend on whether the transition occurs rapidly according to ZND theory. The question is whether shock-loading conditions give sufficient time for the nucleation and growth of a new phase before the reaction starts to chemically alter and consume the HMX. Like shock loading, ICE loading also has the ability to dynamically probe phase transitions at high strain rate and yet it has the potential to achieve significantly higher pressures without provoking reaction in the sample [2].

Experimental Procedure

There are numerous excellent references on the ICE technique so this will not be described in detail here [3,4]. Very briefly, an enormous electrical current pulse is used to drive a compressive ramp wave in a conductive aluminum substrate via the Lorentz force.

This ramp wave (duration approximately 200 ns) propagates from the substrate into HMX samples of carefully quantified thickness, ranging from about 400 to 600 μm in thickness. The HMX samples [5] were of two crystal orientations (010) and (110) and were tamped using optically transparent windows (PMMA, LiF (100), and NaCl (100) were all used in this particular experiment). The velocity of the respective HMX/window interface was measured with VISAR interferometry equipment from VALYN VISAR. Peak interface velocities on the order of 2.5 km/s were obtained in the case of NaCl windows and 2.1 km/s in the case of LiF windows, indicating that the peak stress achieved was on the order of 37 GPa in the HMX sample interior. Using the current history, the VISAR data, and detailed thickness measurements of aluminum substrate and HMX samples, the VISAR data are simulated using the Trac-II magnetohydrodynamic code.

Discussion

In order to assess accurately the occurrence or absence of the phase transition it is important to be able to model it. An HMX loading curve based on the QEOS fit of the isotherm data is used [6,7]. Although the 12 GPa (β to ϵ) transition will probably not show up in VISAR records due to its lack of volume dependency, the 27 GPa transition should show up if it occurs. Our use of the QEOS form assumes that the transition goes to completion instantaneously.

Comparison of simulation to experiment for the (110) orientation of HMX using LiF (100) windows shows no obvious indications of a phase transition for this orientation. On the other hand, in Fig. 1 we see that the data for the thicker sample of the (010) HMX orientation shows some hint of anomaly at about 2.1 km/s, but it is not nearly at the level indicated in the simulation, suggesting that the transition may be sluggish and very incomplete on the time scale of the experiment.

One complication is that we used NaCl windows for our (010) HMX data. NaCl is known to have a phase transition at 26 GPa [8], close to the HMX phase transition.

To further investigate the possible influence of NaCl, we deduced an accurate pressure drive for simulations using the D.B. Hayes backwards integration technique [9] on VISAR data from a reference interface consisting of LiF (100) window directly on the aluminum substrate. The Al/LiF deduced pressure drive above was used in Trac-II to simulate the VISAR data from a NaCl (100) window directly on the substrate. These simulations uses a simple linear NaCl Hugoniot equation-of-state lacking any phase transition information. The Al/NaCl simulation and Al/NaCl data displayed in Fig. 2 disagree at about 2.1 km/s. Figure 3 tells the same story in another way: Here the Al/NaCl VISAR data were backward integrated to obtain a pressure drive and then compared with the more reliable aforementioned pressure drive deduced from the phase-transition-free Al/LiF VISAR data. Lacking a phase transition in NaCl the two drives

should be identical within experimental and computational uncertainties. The discrepancies illustrate that the phase transition in the NaCl window can obscure accurate observations regarding a 27 GPa phase transition in HMX.

It should be pointed out that the lack of evidence for a phase transition in the (110) data does not negate the possibility of its occurrence in the (010) or other orientations as there are examples where the crystal orientation relative to wave propagation direction is believed to be an important factor in successfully inducing phase transformation, as in KCl [11], graphite to diamond [12], and CdS [13].

Finally, we derived a best-fit linear Hugoniot for unreacted HMX based on our HMX (110) data using Trac-II simulations. The constant gamma/volume assumption was used with a Γ_0 of 1.20 based on thermodynamic data from the literature. The Hugoniot given by $U_s = 3.45 \text{ km/s} + 1.90 * U_p$ fit our data well in the range up to interface velocities of 1.7 km/s. By contrast, a Hugoniot computed by a least squares fit of existing shock compression data from Los Alamos [12] for both solvent pressed HMX (density 1.891 g/cc) and single crystal HMX (density 1.900 g/cc) gives $U_s = 3.31 \text{ km/s} + 1.55 * U_p$. Further work is needed to satisfactorily obtain an accurate unreacted Hugoniot at high pressures

.

In summary, both the (110) and (010) orientations of HMX have been taken up to 37 GPa using the ICE technique. If the 27 GPa ϵ to ϕ phase transition in HMX does indeed occur, it is sluggish. The (010) orientation needs to be re-examined using LiF windows, which

do not have the additional complication of having their own phase transition as the NaCl does.

Acknowledgements

We would like to acknowledge the outstanding technical assistance of Allen J. Elsholz and Frank Garcia of Lawrence Livermore National Laboratory as well as the technical staff of the Z-machine facility at Sandia National Laboratories. We would like to thank Dennis B. Hayes for helpful discussions. Y.M. Gupta made us aware of relevant works on shock induced phase transitions. We thank R.J. Simpson and P.T. Springer of LLNL for critical funding and support for U. S. DOE by UC, LLNL contract W-7405-Eng-48.

- [1] C-H Yoo and H. Cynn, J. Chem. Phys., **111**, 10229 (1999)

- [2] D.E. Hare, D.B. Reisman, F. Garcia, L.G. Green, J.W. Forbes, M.D. Furnish, Clint Hall, and R.J. Hickman in *Shock Compression of Condensed Matter- 2003*, edited by M.D. Furnish (AIP, Melville NY, 2004).

- [3] D.B. Reisman, A. Toor, R.C. Cauble, C.A. Hall, J.R. Asay, M.D. Knudson, M.D. Furnish, J. Appl. Phys. **89**, 1625 (2001).

- [4] C.A. Hall, J.R. Asay, M.D. Knudson, W.A. Stygar, R.B. Spielman, T.D. Pointon, D.B. Reisman, A. Toor, R.C. Cauble, Rev. Sci. Inst. **72**, 3587 (2001).

- [5] H.H. Cady and L.C. Smith, Studies on the polymorphs of HMX, LAMS-2652 (TID-4500, 1961)
- [6] R.M. More, K.H. Warren, D.A. Young, and G.B. Zimmerman, Phys Fluids **31**, 3059 (1988).
- [7] D.A. Young and E.M. Covey, J. Appl. Phys. **78**, 3748 (1995).
- [8] J. Wackerle and H.L. Stacy in *Shock Compression of Condensed Matter – 1989*, edited by S.C. Schmidt, J.N. Johnson, L.W. Davidson (Elsevier Science Publishers B.V., 1990)
- [9] D.B. Hayes, Sandia National Laboratories Report, SAND2001-1440 (2001).
- [10] “LASL Shock Hugoniot Data”, edited by S.P. Marsh (U. California Press, Berkeley, 1980). p.335, 595-6
- [11] D.B. Hayes, J. Appl. Phys. **45**, 1208 (1974).
- [12] D.J. Erskine and W.J. Nellis, Nature **349**, 317 (1991).
- [13] M.D. Knudson and Y.M. Gupta, J. Appl. Phys. **91**, 9561 (2002).

Figure captions

Figure 1: (010) HMX with NaCl window, VISAR data versus Trac-II simulation using QEOS for HMX. The velocity is given in cm/ μ s.

Figure 2: Simulation of the Al / NaCl VISAR interface versus the actual data record. The phase-transitionless linear Hugoniot EOS was used to simulate the NaCl. The velocity is given in cm/ μ s.

Figure 3: Comparison of the pressure drives created by the backward integration of the Al/NaCl and Al/ LiF VISAR records. The linear Hugoniot was used for the NaCl. The pressure is given in Megabar.

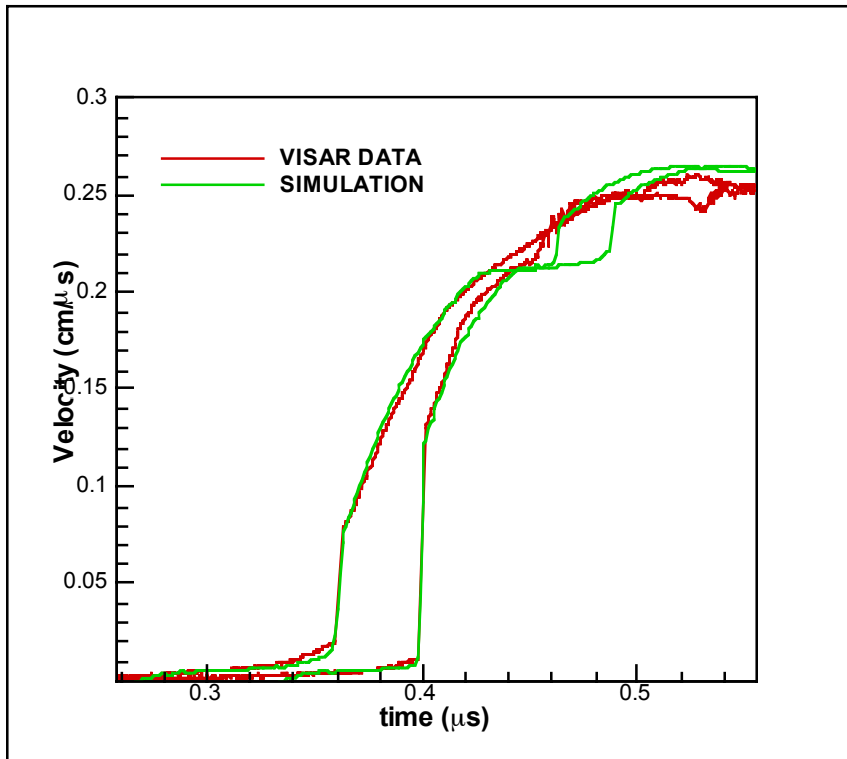


Figure 1

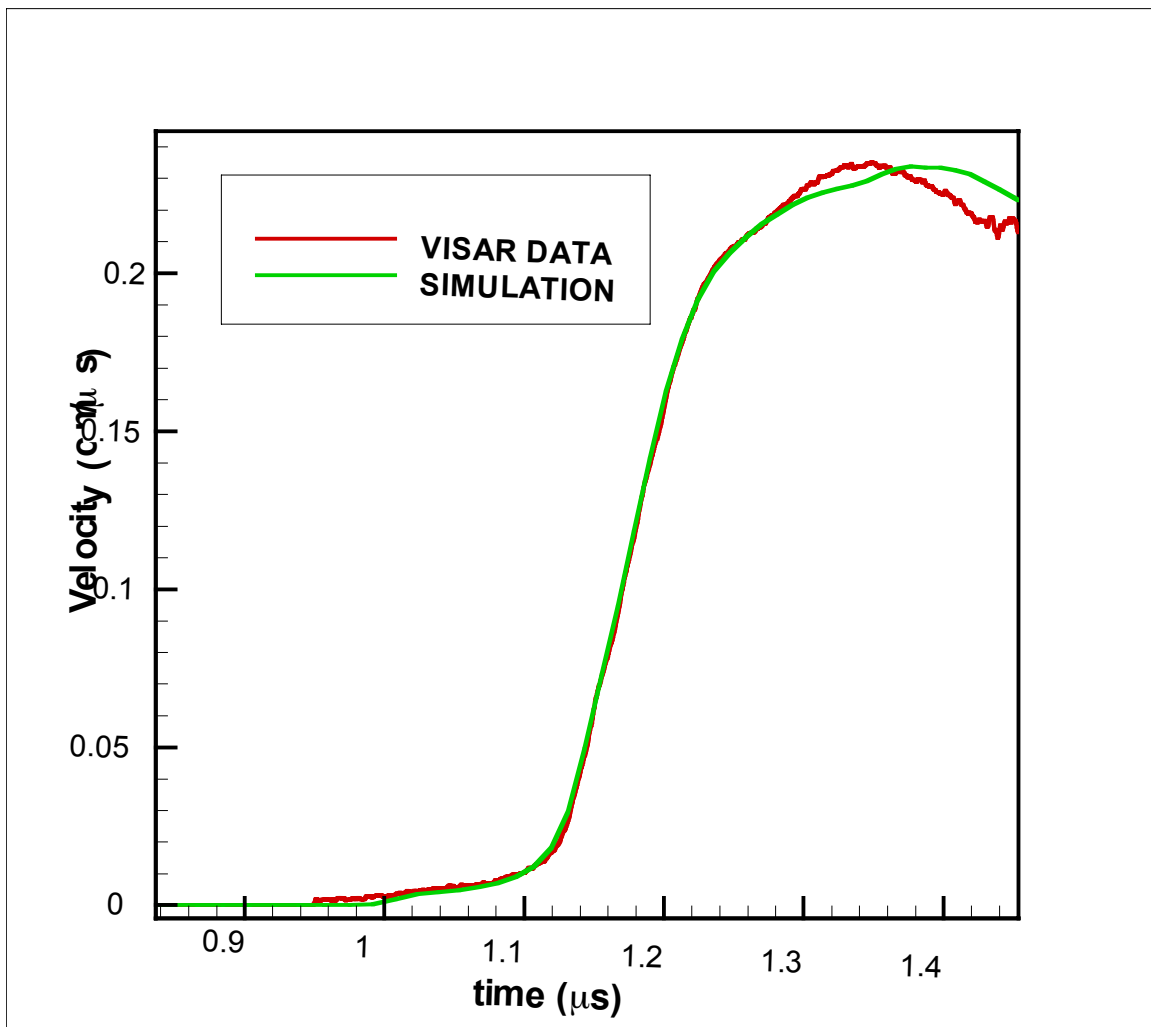


Figure 2

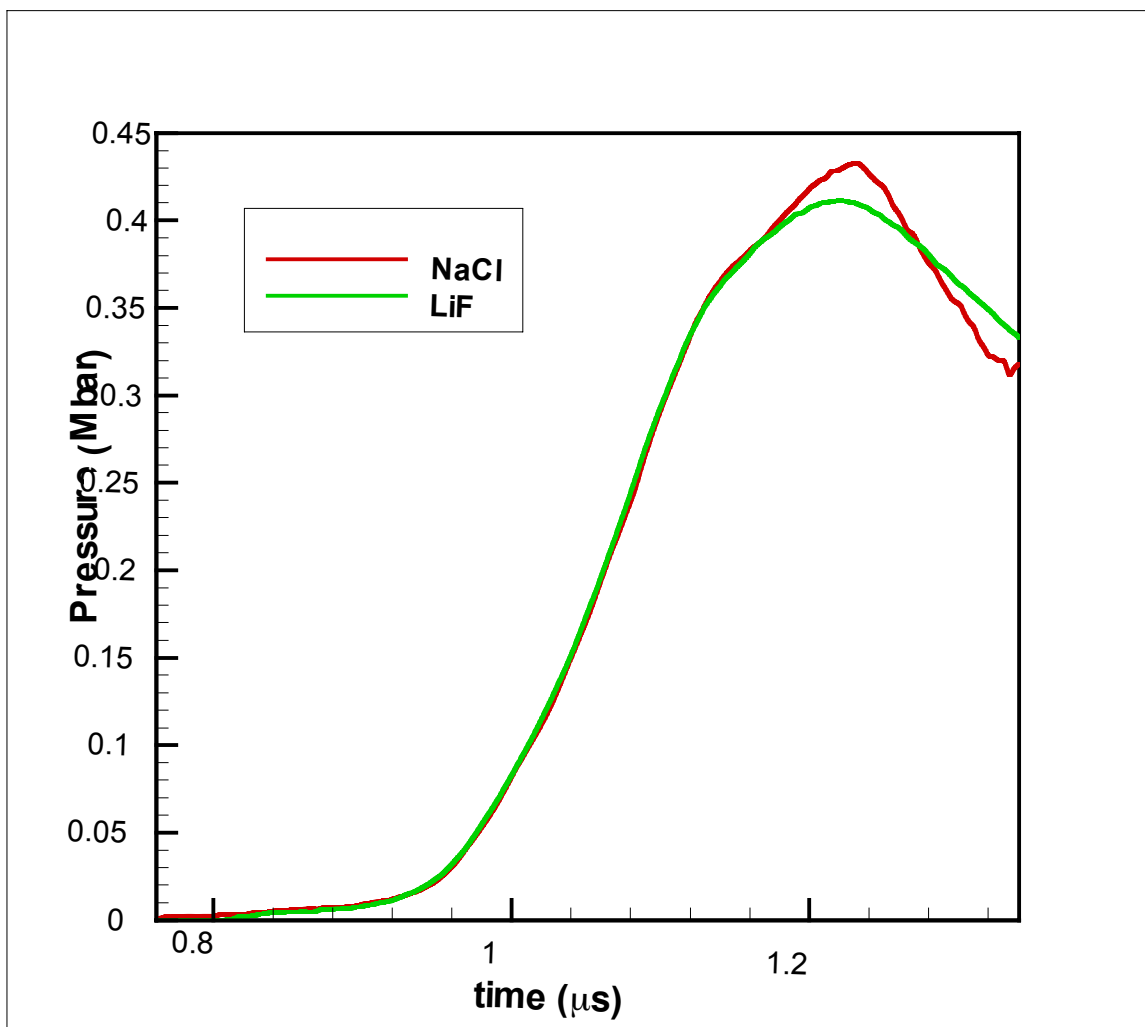


Figure 3